POLYPROPYLENE REINFORCED WITH NANOCLAY CLOISITE® 30B: STUDY ON MECHANICAL PROPERTIES.

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ABSTRACT

Polymer had been widely use nowadays in many field. Their properties make them useful in much industrial activity, such as coating, packaging labels and etc. The escalating of world technology requires improvement in the existing polymer. Hence, polymer composites had been invented to fulfil the need. Polymer nanocomposites are one of the latest technologies invented to enhance the targeted polymer in many site such as mechanical properties, thermal properties, electricity conductivity and etc. In this study, polypropylene (PP) had been chosen to be modifying by adding 30B organoclay to increase its mechanical properties. By using melt intercalation method, twin screw extruder has been used to prepare the sample. The sample differentiates each other by their amount of nanofiller. Starting with the pure PP, and three other sample (1wt%, 3wt% and 5wt% of nanofiller) were prepared by the same method. The introduction of 30B organoclay in PP had shown the increment of its properties in their mechanical properties. In testing its hardness, Rockwell-Brinell hardness test had been performed. The test uses the indentation value to show its hardness. The result showed that the hardness had been increase up to 32.9%. The tensile strength of produced composite also had been test to see the differences between the pure polymer and the nanocomposites. The tensile strength analysis applied stress to the sample until its maximum load. The results indicate that its strength had been improved up to 207% with addition of nanofiller. To ensure the improvement of the sample is because of the nanofiller, FTIR analysis had been run to show the existence of the nanofiller itself. The introduction of nanofiller in the polymer nanocomposites had proved a significant improvement in the mechanical properties.

ABSTRAK

Polimer telah digunakan secara meluas saat ini dalam pelbagai bidang. Sifat mereka membuatkan mereka berguna dalam pelbagai kegiatan industri, seperti penyadur, label bungkusan dan lain-lain. Peningkatan teknologi dunia memerlukan penambahbaikan dalam polimer yang sedia ada. Oleh kerana itu, komposit polimer telah dicipta untuk memenuhi keperluan tersebut. Polimer nanokomposit adalah salah satu teknologi terkini dicipta untuk meningkatkan polimer yang diberi tumpuan dalam pelbagai aspek merangkumi sifat mekanik, sifat terma, konduktiviti elektrik dan lain-lain. Dalam kajian ini, 'polypropylene' (PP) telah dipilih untuk menjadi subjek dengan menambah 'organoclay 30B' untuk meningkatkan sifat mekanikalnya. Dengan menggunakan kaedah pencairan interkalasi, skru ekstruder berkembar telah digunakan untuk menghasilkan sampel. Sampel membezakan antara satu sama lain dengan jumlah 'nanofiller' mereka. Dimulai dengan PP asli, dan tiga sampel lain (1wt%, 3wt% dan 5wt% 'nanofiller') dihasilkan dengan kaedah yang sama. Pengenalan '30B organoclay' dalam PP telah menunjukkan peningkatan dalam sifat mekanik mereka. Dalam ujian kekerasannya, 'Rockwell-Brinell' ujian kekerasan telah dilakukan. Ujian menggunakan nilai lekukan untuk menunjukkan kekerasan itu. Keputusan kajian menunjukkan bahawa kekerasan telah meningkat hingga 32,9%. Kekuatan tarik komposit yang dihasilkan juga telah diuji untuk melihat perbezaan antara polimer asli dan nanokomposit. Analisis kekuatan tarik diterapkan tekanan ke atas sampel sehingga beban maksimum. Keputusan kajian menunjukkan bahawa kekuatan sampel telah meningkat sehingga 207% dengan penambahan 'nanofiller'. Untuk memastikan peningkatan sampel adalah kerana nanofiller, analisis FTIR telah dijalankan untuk menunjukkan kewujudan nanofiller tersebut. Pengenalan nanofiller dalam polimer nanocomposites telah membuktikan peningkatan yang signifikan dalam sifat mekanik.

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LIST OF ABBREVIATION

PP	-	Polypropylene
PNC	-	Polymer Nanocomposite
FTIR	-	Fourier-transformed infrared spectrophotometry
kgf	-	Kilogram Force
N	-	Newton
kN	-	Kilonewton
mm	-	Millimeter
PVC	-	Polyvinyl Chloride
EPDM	-	Ethylene Propylene Rubber
PP	-	Polypropylene
LLDPE	-	Linear Low-Density Polyethylene
MDPE	-	Medium-Density Polyethylene
HDPE	-	High- Density Polyethylene
AAS	-	Atomic Absorption Spectroscopy
XRF	-	X-Ray Fluorescence Radioisotope
Ca	-	Calcium
EDTA	-	Ethylene-Diamine-Tetra-Acetic
FLAA	-	Flame Atomic Absorption Spectrometry
GFAA	-	Graphite Furnace Atomic Absorption
ICP-AES	-	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	-	Inductively Coupled Plasma Atomic Emission Spectrometry
ppm	-	Part Per Million

Chapter 1

INTRODUCTION

1.1 Research Background

Polypropylene is one of the common polymers used nowadays in almost all industrial fields such as automotive technology, food industry and etc. The useful properties possessed by this polymer are the main reason for its popularity in the industrial field. Low molecular weight, low density, cheap, easily produce and its resistance to corrosion is a few reason for polypropylene to be widely use in those industrial field.

Polypropylene is one of the thermoplastic which produced by its linked chain of its monomer, propene. The structure can be classified into two types, which are isotactic and syndiotactic. These two arrangements in the polypropylene backbone tend to coil and form the helical shape is what brings the desire mechanical properties by the world technology. As for the strong bond between its monomer, polypropylene did not dissolve in water, hence bring the effect of water proof. The low density it possessed make the structure made out of it light yet durable. The corrosion resistance ability is very helpful in coating industry. In general, the chemical property it has is very handy and make it the priority in the industrial field. Due to the low manufacturing cost, it adds up every reason for industrial site to choose this polymer.

When the world extends its technology, the need for better polymer arises. Polypropylene is one of the polymers that are subjected to have upgrade and modification. By using composite technology, polypropylene received improvement in its chemical and mechanical properties. Addition of fiber in different of type, reinforce its properties.

As the world keeps moving forward in technology, polymer composite becomes conventional polymer that commonly use. New finding have been made and polymer nanocomposite have been given birth. This nanocomposite is the new breath in the world of polymer. Many intelligent researchers have gather and share their intelligence in producing nanocomposite with variety of nanofiller, which improve the polymer in different ways. Until today, nanocomposite still being study and new founding keep appearing.

Polymer nanocomposite had given a significant improvement compare to the conventional polymer. The improvement in microstructure improves the polymer nanocomposite properties down to the micro scale. The addition of nanofiller such as clay particle and carbon nano tube, improve the properties more than 50%. Despite of its significant improvement, its low density, low weight, and acceptable cost are the reasons why its been popular day by day. The polymer nanocomposite also has widen the area of it application. Now, it can be use in microstructure which applied in modern equipment.

In this study, polypropylene-clay nanocomposite is subjected to be the interest to focus on. There is much reason on why polypropylene had been chosen. Among them are because of it low cost and widely use in many industrial field. From previous study, the tensile strength of polypropylene had been boosted with the reinforcement of nanoclay. The nanocomposite arrangement of polymer matrix between the clay layer form interaction between them. The strong hydrogen bond between them make the polymer tensile properties increase (Thac KimN et al.,2006, Saminathan K. et al., 2008).

The arrangement of nanocomposite can be distinguish into three types. There are intercalated nanocomposites, flocculated nanocomposites, and exfoliated nanocomposites (Wypych and Satyanarayana, 2005; Ray and Okamoto, 2003). Each of them brings different effect on the properties improvement. The arrangement of the nanocomposite can be achieved by using different type of method in producing the particular polymer (Sharma et. al, 2004).

There are three main method use in producing the polymer nanocomposite which are intercalation of polymer or pre-polymer from solution, in situ intercalative polymerization method and melt intercalation method. Each of the method will bring different type of nanocomposite arrangement. Out of the three methods, the interested one that will be use in this study is the melt intercalation method. The method is the simplest, low cost, widely use in industrial field and nature friendly.

Previous study on the propylene-clay nanocomposite showed significant improvement in the mechanical properties. The improvement is up to 50% in the mechanical properties. This is a significant value and need to look further into consideration in the clay content in the nanocomposite.

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1.2 Objective

The aim of this research is to study the mechanical properties of Polypropylene-clay nanocomposite and comparing it to the pure Polypropylene.

1.3 Scope of Study

To achieve the objective of the study, a number of scopes have been drawn to be fulfilled:

1. To produce Polypropylene and Polypropylene organoclay nanocomposite using melt intercalation method using the twin screw extruder.
2. To characterize the properties and morphology of Polypropylene organoclay nanocomposite using Fourier Transform Infra Red (FTIR) and Scanning Electron Microscopy (SEM).
3. To study the mechanical properties which are tensile strength and hardness of the polypropylene organoclay nanocomposite.

1.4 Problem statement

The world won’t stop stepping forward in advancing its technology. In developing the overall technology, polymer industry also need to be modernize to balance the growth. This is because polymer is one of the incredible founding mankind ever made and it’s needed in almost every other technology. When there is a need, a solution for the particular need have to solve. The latest technology in polymer industries would be the polymer nancomposite where it is proven to have significant advantages compared to the pure polymer, ready to gear up the technology growth once again.

A lot research had been done on this topic, but not all of them able to produce the desire product. The composition of the composite had to be study to have a perfect blend. The morphology of the polymer also needs to be taken care as it affects the properties later. By changing intercalation and exfoliation of filler had already brought significant differences in the properties. The composition and the method in producing the polymer nanocomposite must be in the first priority in producing the desire product.

1.5 Rationale and significant

This study is designed to enhance the properties of Polypropylene which reinforced by the existence of the organoclay 30B. With the new polymer produced, much benefit can be obtained by the food industry, agriculture, construction and even automotive industry. With the outstanding performance of the new polymer, the other industry can receive its benefit and continue in stepping ahead.

In producing the PP/organoclay nanocomposite, organoclay will be consumed. Although the filler comes with high price, but it is still manageable because we only need a small portion of it. Considering the improvement it brings, we can say that producing this PP/organoclay is still economical.

CHAPTER 2

THE PHYSICAL AND CHEMICAL PROPERTIES OF POLYPROPYLENE AND POLYPROPYLENE-CLAY NANOCOMPOSITES

2.1 Introduction

Polymer is one of the materials in this world that would not stop in development. They keep improving in structure as well as their properties. From basic based polymer, they have been improved into polymer composite. In the world of polymer composite, the enhancement in structure goes to the macro-scale only. As their structure improves, the properties they possessed also improve to a certain level.

As technology keep advancing, polymer now required in micro-scale application. The problem with this need is polymer composite is not ready to be used in micro-scale technology. The macro-structure of polymer composite is the main reason for this failure. Basic polymer could be use, but it does not fulfil the requirement in their properties. Intelligent researcher had gather and come with a solution, which is to produce polymer nanocomposite. As for it title, nanocomposite use nanofiller to make make them polymer nanocomposite. With this solution, improvement in microstructure can be achieved. The improvement in their properties also down to the microturcture of the particular polymer.

2.2 Polypropylene (PP)

Polypropylene (PP) or well known as polypropene, is actually a type of thermoplastic polymer. Most commercial PP is isotactic and has an intermediate level of crystallinity between that of low-density polyethylene (LDPE) and high-density polyethylene (HDPE). It is widely use in many application included laboratory equipment, packaging, textile and etc.

Polypropylene is first polymerized by Giulio Natta and his coworkers in March 1954 in form of crystalline isotactic polymer **(**Peter J. T. Morris, 2005). This polymer is a linked chain of its methyl group, propene. The important concept in polymerized PP is the link between the structure of polypropylene and its properties is tacticity. The relative orientation of each methyl group (CH_3) relative to the methyl groups in neighboring monomer units has a strong effect on the polymer's ability to form crystals. There are two types of orientation of methyl group in the polymer, isotactic and syndiotactic. In isotactic orientation, all the methyl group neighboring aligns at the same side with respect of the polymer backbone of the polymer chain. Such isotactic macromolecules will coil into helical shape. These helices shape line up to one another to form crystal and give PP most of its desire properties. The syndiotactic orientation has the methyl group alternately at the polymer’s backbone. Same as the isotactic form, the chain will coil into helical shape and line up to be crystalline material.

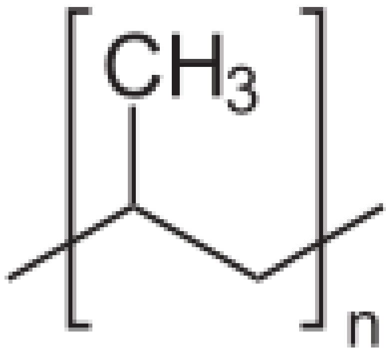

Figure 2.1: Methyl Group

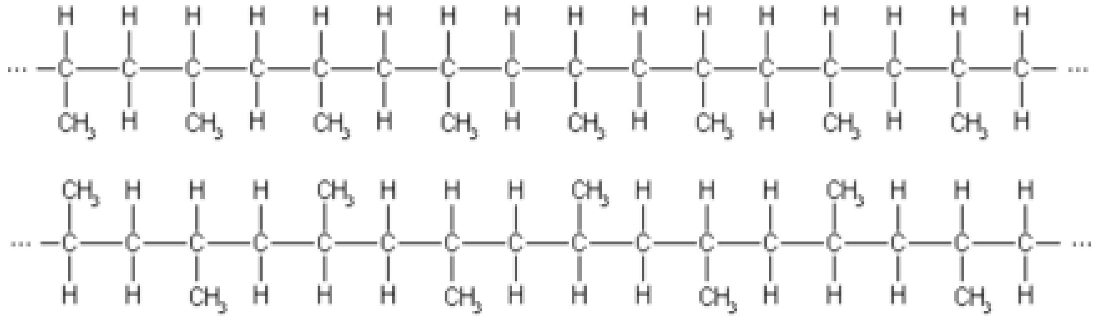

Figure 2.2: Isotactic and syndiotic orientation

2.3 Nanocomposite

In the world of composites, the particular material having two or more distinct phases such that a better combination of properties is achieved. Before go any further about nanocomposite, Let review what is composite really are. Composite materials are materials having two or more distinct phases such that a better combination of properties is achieved. The constituents must be chemically and physically dissimilar and separated by a distinct interface. The composite consists of a matrix, which is continuous and surrounds the filler, which provides the reinforcement such that the resulting composite property is a function of the properties of both the matrix and filler. The constituents will retain their identities; they do not dissolve or merge completely into one another although they act as one.

The components can be physically identified and show an interface between one another. So, for a nanocomposite material, it is still a composite but despite of the macroscale mentioned before, it comes in a size of below than 100 nm.

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials.

Size limits for these effects have been proposed:

Effect	Size limit (nm)
Catalytic activity	< 5
Hard magnetic material to soft material	< 20
Refractive index changes	< 50
Achieving superparamagnetism / mechanical strengthening / matrix dislocation movement	< 100

The following is the most common techniques for the synthesis of polymer nanocomposite:

1. *In situ polymerization*; where the fillers are initially dispersed in the monomer, followed by the polymerization of the monomer within the fillers gallery.
2. *Melt intercalation*; where the polymer molecules, intercalate the fillers layers during the melt processing.
3. *Intercalation in polymer solution*; where the fillers is dispersed in a polymer solution, following by the evaporation of the solvent.

2.4 Nanoclay (Cloisite® 30B)

Cloisite® and Nanofil® additives consist of organically modified nanometer scale which layered by magnesium aluminum silicate platelets. The silicate platelets that the additives are derived from are 1 nanometer thick and 70 – 150 nanometers across. The platelets which are originally normal clay are surface modified with an organic chemistry to allow them to complete dispersion into and provide miscibility with the thermoplastic systems for which they were targeted to improve. The additives have been proven to reinforce thermoplastics by enhancing flexural and tensile modulus. The additives have also been proven to be effective at improving gas barrier properties of thermoplastic systems. The surface char formation and flame retardance of thermoplastic systems have also been improved by incorporating the nanoparticles into the structure. There are some unique application areas where the additives have been proven to improve the physical properties of the plastic products. Cloisite® and Nanofil® additives have been shown to improve the properties of injection molded pieces for the automotive industry, of flexible and rigid packaging such as films, bottles, trays, and blister packs, and also of electronics plastics such as wire and cable coatings.

Figure 2.3: SEM graphic focusing on nanoclay particle.

2.5 Polymer Nanocomposite

2.5.1 Introduction

Polymer which had been used for generation beholds a great potential to be improve. Previously, intelligent researcher had found the way to strengthen them by turning them into composite. By adding fillers such as fiber manages to improve their mechanical or chemical properties or both. Nowadays, there is a new way found to improve polymer properties, by using nanofiller to make them nanocomposite.

Main feature of polymeric nanocomposite, which differ it with the conventional composite, lies in the reinforcement on the order of nanometer which greatly affected to the final macroscopic properties. Polymeric nanocomposites can be produce with different particle nanosize, nature and shape:

- Clay/Polymer Nanocomposites
- Metal/Polymer Nanocomposites
- Carbon Nanotubes Nanocomposites

There are three main material constituents in any composite: the matrix, the reinforcement (filler), and the so-called interfacial region. The interfacial region is responsible for communication between the matrix and filler and is conventionally ascribed properties different from the bulk matrix because of its proximity to the surface of the filler (Vaia and Wagner, 2004).

In mechanical view, nanocomposites differ themselves from conventional composite materials due to their high surface to volume ratio of the reinforcing phase. The reinforcing material can be made up of particles, sheets, or fibers. The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Local chemistry, polymer chain mobility and polymer chain conformation is what basically affected the polymer nanocomposites properties. The degree of polymer chain ordering can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

Polymer nanocomposite represents a radical alternative to conventional filled polymers or polymer blends – a staple of the modern plastics industry. In contrast to conventional composites, where the reinforcement is on the order of microns, PNCs are exemplified by discrete constituents on the order of a few nanometers. The value of PNC technology is not solely based on the mechanical enhancement of the neat resin nor the direct replacement of current filler or blend technology. Rather, its importance comes from providing value-added properties not present in the neat resin, without sacrificing the resin’s inherent processibility and mechanical properties, or by adding excessive weight. PNCs contain substantially less filler (1-5 vol %) and thus enabling greater retention of the inherent processibility and toughness of the neat resin (Vaia and Wagner, 2004).